THE ANALYST.

SEPTEMBER, 1892.

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS.

NOTES FROM THE KHEDIVIAL LABORATORY.

Read at Meeting, June 1st, 1892.

By H. Droop Richmond (late Second Chemist to the Egyptian Government).

7. On a Sample of Milk yielded by an Arab Woman.—Although the analysis of isolated samples of milk cannot be accepted as giving much definite information, still I think that it may not be without interest to record the analysis of a sample of milk yielded by an Arab woman. It was one of two samples sent by a medical man for the purpose of judging which would be most suitable for an infant. As far as I can find, no milk of Arab women has been analysed, and it is still an open question as to whether race has any influence on the composition of milk in the human subject as it has in the cow. Probably, personal differences have much more influence; and I therefore recorded the analysis without further comment:—

Water	85·92
Fat	5·31
Sugar	6·41
Proteids*	2·16
Ash	·20
	100·00

* Containing Nitrogen ... ... ·339

8. Egyptian Flour.—As, as far as I can find, no analyses of Egyptian flour have been published, the following may be of interest. It is considered a very inferior flour, and although imported in fair quantities into England, is not used for bread-making, but rather for the manufacture of starch.

It is very rare to find Egyptian flours which, on microscopic examination, do not show the presence of a leguminous starch, and also often of "doura" or maize; probably, the presence of "doura" is as frequent as that of the leguminous starch; but it is difficult to detect in small quantities, it resembling very much the wheat starch, but giving a much

more distinct cross in water when examined by polarised light. These foreign starches, in such small quantities as to preclude the idea of adulteration, I have found in samples which have come from sources which almost entirely exclude suspicion, and their presence is due to the fact that very little care is taken to prevent the accidental occurrence of the foreign starches, wheat being ground in the same mill in which "doura" or "fool" (beans) have been previously ground, with only a superficial cleaning. It is also of not unusual occurrence to find husk in considerable quantities and dirt.

The only method of analysis which needs discussion is the estimation of the soluble constituents. Ten grammes of the flour are shaken with 250 c.c. of water at 15° for an hour, the temperature being kept as constant as possible, and then allowed to stand four hours, at the expiration of which the solution is filtered, and in it are estimated the total solids, ash, nitrogen, nitrogen in tannin precipitate, and acidity as lactic acid. The following figures have been established:—

For the total solids in good flours, from 5 to 6 per cent., going up to nearly 10 per cent. in inferior samples.

The ash is about 10 per cent. of the total solids, being slightly less in good samples and more in bad.

The total soluble nitrogen, and that in the tannin precipitate, are practically the same in good samples, while in inferior ones there is a difference of nearly ·1 per cent.

The character of the tannin precipitate differs in good and bad samples, being in good ones whiter and more voluminous than in bad ones, in which it takes a brownish pink hue.

The following figures were obtained in four typical samples:—

	Good.	Moderate.	Bad A.	Bad B.
Moisture	11·63	11·70	8·35	9·50
Ash	·65	1·72	1·80	1·92
Gluten	7·61	7·58	8·21	8·06
Soluble Albuminoids... ...	1·28	1·56	1·39	1·41
Non-Albuminoids	Trace	·10	·17	·24
Cellulose	·44	·49	·63	·59
Starch (difference)	72·05	67·57	70·96	70·04
Amylan, Sugar, &c.	4·16	6·14	6·04	6·50
Fat	2·18	3·14	2·45	1·74
	100·00	100·00	100·00	100·00
Soluble in Water	5·88	8·68	8·58	9·12
Ash	·44	·88	·97	·97
Nitrogen	.205	·283	·278	·305
Nitrogen in Tannin ppt. ...	·203	·250	·222	·225
Total Nitrogen	1·423	1·500	1·591	1·584
Phosphoric Acid in Ash ...	·27	·60	·56	·81

9. Some Egyptian Waters.—The great source of water in Egypt is the Nile, and of the water of the Nile I shall speak at another time; in this note I propose only to touch on a few waters not directly connected with the Nile.

The waters I have to speak of can be divided into two classes, (*a*) those probably having filtered from the Nile through a considerable distance, and (*b*) those probably having no connection with the Nile.

In order to compare these I give the average (mineral) composition of the Nile water:—

Silica, Fe_2O_3, &c.	·976
Lime	4·218
Magnesia	1·005
Potash	1·437
Soda	·584
Chlorine	·755
Sulphuric Acid...	2·170
Carbonic Acid	3·843
Nitric and Phosphoric Acid	None, or very faint traces.
	14·988
Less O=Cl	·170
	14·818

The two first waters of which I wish to speak come from near Cairo. The first is a shallow well water in Cairo, about a mile and a-half from the Nile, in the Ezbekieh quarter, and may be taken as a typical one; the second is from a deep boring at Mena House Hotel, under the shadow of the Great Pyramid, about 8 miles from Cairo and 6 miles from the Nile. Both are remarkable for their great organic purity and the considerable amount (in Egypt) of nitrates; indeed, the water of the Mena House Hotel is the purest I have ever examined.

The analysis is as follows:—

	No. 1.	No. 2.
Free Ammonia	·013	None
Albuminoid Ammonia	·005	None
Oxygen absorbed 15 min.... ...	·021	·003
„ „ 4 hours... ...	·057	·053
Total Solids	101·28	25·96
Loss on Ignition	8·32	·60
Silica	4·68	2·83
Oxide of Iron, &c....	·40	·30
Lime	12·30	6·27
Magnesia	7·99	2·38

Potash	11·35	·61
Soda	18·49	2·48
Chlorine	8·91	2·53
Nitric Acid	·73	·65
Sulphuric Acid	17·40	·95
Carbonic ,, ...	21·72	7·22
	103·97	26·23
Less Oxygen=Chlorine	2·01	·57
	101·96	25·66

The first water has evidently taken up considerable amounts of salts during its passage from the Nile, salts probably having their origin from the same river. The silica is very high.

The second water has taken up much less salts, and a doubt has arisen as to whether it is Nile water, for the following reasons:—It contains much less potash and sulphuric acid than the Nile, and it is difficult to see how these bodies have been lost, as it flows through a country almost devoid of vegetation. It is below the level of the Nile, and its rise and fall does not coincide with that of the Nile, but follows it at a considerable period and to a limited extent; unless we admit that it has travelled hundreds of miles underground, and certain other considerations render this unlikely, it can have no other source than the Nile. It comes up through limestone, and sometimes has a tendency to deposit chalk, which it takes up again on exposure to the air; the uncombined carbonic acid is very small, ·88 parts per 100,000.

I am of opinion that it has no connection with the Nile at Cairo, but has its source higher up.

A third water, which may be taken as typical of the non-sulphurous waters of Helouan, 20 miles above Cairo:—

Silica	1·8
Oxide of Iron, &c.	1·4
Lime	60·8
Magnesia	57·1
Potash	1·4
Soda	298·0
Chlorine	417·4
Sulphuric Acid	97·5
Carbonic Acid...	11·0
	946·4
less Oxygen=Chlorine	94·0
	852·4

Density, 1·0067.

This is simply the Nile water which has taken up a quantity of the native salt, which abounds at Helouan, and calls for no remark.

The sulphurous waters of Helouan have been ably treated of by Prof. Gastinel Pasha (Etude sur les Eaux Thermales de Helouan).

In class (b) as typical of the saline waters which occur at Mex, Edko, Bourloss, and other places on the North of the Delta and near Suez, may be taken that of Shaloof (near Suez).

As it is very highly concentrated (having a density of 1·1939), the results are expressed as percentages, and not as parts per 100,000. It is quite saturated with salts, and agrees very closely in composition both with concentrated sea water and with other saline waters of Egypt; there is no doubt that these waters are derived from the sea, and they are the origin of the salt industry.

No. 4.

Water	75·660	Water	75·660
Silica	·002	SiO_2	·002
Oxide of Iron, &c. ...	Traces	Fe_2O_3, &c.	Traces
Lime	·627	$CaSO_4$	·163
Magnesia	1·281	$CaCl_2$	1·110
Potash	·120	$MgCl_2$	3·024
Soda	10·497	NaCl	19·808
Chlorine	15·076	KCl	·190
Bromine	·030	$MgBr_2$	·034
Iodine	Traces		
Sulphuric Acid ...	·096		99·991
	103·359		
Less oxygen = Cl and Br.	3·370		
	99·989		

The next two waters occur in a cave at Bahnesa, about 10 miles to the West of Minieh, and were taken at two different times this water is about fifteen feet above the Nile, and its source, which is unknown, is probably not that river. The analyses are :—

	No. 5.	No. 6.
Silica	1·96	2·20
Oxide of Iron, &c.	·64	·20
Lime	21·16	17·81
Magnesia	14·98	15·57
Potash	73·08	77·68
Soda	31·07	29·11
Sulphuric Acid	26.68	21·32

Chlorine	122·57	121·37
Carbonic Acid	none	1·19
	292·14	286·45
Less Oxygen = Chlorine ...	27·68	27·45
	264·46	259·00
Acidity as HCl	1·14	None

These waters are remarkable; first, for the large quantity of potash they contain; second, for the fact that the first is *acid*, while the other is not; what the significance of this fact is I know not; it may indicate coal with its attendant pyrites, or possibly volcanic sulphur.

In the same district, although many miles away, occur, a water containing ferrous carbonate, which of course oxidizes and deposits, and which is used as a tonic; a purgative water containing magnesium, sodium and potassium sulphates; a water reputed to cure syphilis; and a water said to have the power of dyeing red fabrics (alizarin?) black; these last two I have not had the opportunity of examining.

Appendix. The bases are calculated with the acids as salts.

	Nile.	No. 1.	No. 2.	No. 3.	No. 5.	No. 6.
$Mg(NO_3)_2$	—	1·16	·90	—	—	—
Na_2SO_4	1·337	30·81	1·68	—	—	—
$CaSO_4$	1·780	—	—	—	45·10	36·24
$MgSO_4$	—	—	—	44·7	—	—
K_2SO_4	·806	—	—	115·1	—	—
$CaCO_3$	6·222	21·96	11·19	23·9	—	2·70
$MgCO_3$	2·110	15·88	4·43	—	—	—
K_2CO_3	—	11·75	—	—	—	—
NaCl	—	9·98	3·27	562·4	58·63	54·93
KCl	1·587	5·34	·97	2·2	115·75	123·03
$CaCl_2$	—	—	—	—	5·43	2·73
$MgCl_2$	—	—	·09	100·4	35·58	36·97
$(FeAl)_2Cl_2$	—	—	—	—	·90	—
HCl	—	—	—	—	1·14	—
Fe_2O_3 }	·976	·40	·30	1·4	—	·20
SiO_2 }		4·68	2·83	1·8	1·96	2·20
	14·818	101·96	25·66	851·9	264·49	259·00

10.—Normal Sulphuric Acid, Barium Sulphate, and Decinormal Barium Hydrate.—An approximately normal solution of sulphuric acid was prepared by mixing

90 c.c. of freshly distilled sulphuric acid and three litres of distilled water. As this solution was to serve as the standard volumetric solution, it was standardized with great care.

The density was taken at 15°, 20°, 25° and 30°, with the following results :—

Temp. T.	Density $= D\frac{T}{4^\circ}$
15°	1·03355 1·03356
20°	1·03200
25°	1·03025
30°	1·02835

From the table given by Pickering (*Jour. Chem. Soc.*), the strength of the solution was calculated

from results at 15° ...	...	...	5·062 per cent. H_2SO_4
„ „ 20° ...	...	...	5·061 „ „
„ „ 25° ...	...	...	5·050 „ „
„ „ 30° ...	...	...	5·033 „ „
Mean	...	...	5·051 „ „

Correcting those of Pickering's results which stood nearest to my determinations, the density at 15° corresponded to a strength of 5·071 per cent. H_2SO_4.

Three gravimetric determinations as barium sulphate, using from six to nine grams of the solution gave

	5·102 per cent.
	5·105 „
	5·104 „
Mean ...	5·104 per cent. H_2SO_4

The formula calculated for the strength of the solution from my results is :—

Strength at T° = Strength at 15° [1·0000 — 0·0003 (T — 15°) — 0·0000022 $(T - 15^\circ)^2$]

This formula is probably not strictly exact, but its error is within the limits of titration.

1 c.c. of my normal solution = 0·0431 — 0·000013 (T — 15°) — 0·000000094 $(T - 15^\circ)^2$ grs. SO_3.

Weighed quantities were, however, generally used.

Experiments of the estimation of sulphuric acid and barium as barium sulphate were carried out. As this is not new, I shall not give them in detail ; but as it is highly desirable from time to time to emphasize the precautions necessary to be observed in this most important determination, I give the conclusions :—

(i.) The solution must contain free hydrochloric acid in the proportion of at least 3 HCl to 1 SO_3.

(ii.) An excess of barium chloride must be avoided, and especially crystals of barium chloride must not be used.

(iii.) The solution must be gently boiling, and the precipitant added gradually. I found it best to add a solution of barium chloride (10 per cent.) drop by drop from a pipette to a gently boiling solution, until precipitation seemed complete, to continue boiling gently for ten minutes, to allow to settle, and test with another drop.

(iv.) After precipitation, at least an hour or two's repose is necessary; if the solution is very acid or if the quantity is very small, twenty-four hours, standing should be given.

(v.) The presence of iron, aluminium, and alkaline salts, except in traces, and of nitrates, should be avoided.

(vi.) If ignited slowly at first, and then strongly in a current of air, the precipitate may be burnt with the filter paper.

With these precautions, I believe this determination to be one of the most exact existing. Duplicates need not differ by more than half a milligram.

An approximately decinormal solution of barium hydrate was prepared with three-times-crystallized barium hydrate.

It was titrated with the normal sulphuric acid.

(i.) 3·9152 grs. normal sulphuric acid (5·104 per cent.) = 40·78 c.c. $\frac{N}{10}$ took 39·48 c.c. barium hydrate solution; this gave on evaporation and ignition 0·4791 grs. $BaSO_4$, and the same after ignition with sulphuric acid.

(ii.) 2·9278 grs. N. sulphuric acid solution (5·104 per cent.) = 30·50 c.c. $\frac{N}{10}$ took 29·48 c.c. barium hydrate solution; this gave on evaporation and ignition 0·3589 grs. $BaSO_4$, and the same after ignition with sulphuric acid.

These give the strength for the barium hydrate solution as follows:—

	From Titration.	From $BaSO_4$.
(i.)	0·10330 N.	0·10415 N.
(ii.)	0·10346 N.	0·10440 N.
or mean	0·10338 N.	0·10428 N.

Titrated with pure oxalic acid, the strength of the solution was 0·1042 N.

The titration of barium hydrate solution with standard sulphuric acid is then not accurate.

THE RELATION BETWEEN SPECIFIC GRAVITY, FAT, AND SOLIDS-NOT-FAT IN MILK.

By H. Droop Richmond.

I have collected the results of 328 analyses of milk, and have compared the figures for fat estimated, and that calculated by my "milk scale;" on Table I. are given the results according to percentages of fat.

TABLE I.

Percentage of Fat.	No. of Samples.	Average Error.	Probable Error.	Percentage of results under ·1% to ·2%	over ·2%	Maximum +error.	Maximum —error.
0 to 1	40	+·010	±·080	60·0	40·0	0	·19	·16
1 to 2	11	+·021	±·067	63·5	36·5	0	·13	·13
2 to 2·5	28	+·018	±·082	64·3	28·6	7·1	·19	·22
2·5 to 2·8	33	+·007	±·064	75·8	24·2	0	·18	·17
2·8 to 3·0	21	—·012	±·068	66·7	35·3	0	·17	·16
3·0 to 3·25	29	—·027	±·069	75·9	20·7	3·4	·12	·20
3·25 to 3·5	39	—·012	±·086	74·4	20·5	5·1	·17	·30
3·5 to 3·75	34	—	±·070	76·5	17·6	5·9	·28	·25
3·75 to 4·0	29	+·006	±·091	51·7	44·8	3·5	·18	·28
4·0 to 5·0	37	—·046	±·107	56·8	32·6	10·6	·15	·32
Over 5·0	15	+·008	±·080	60·0	40·0	0	·15	·18
Total	316	—·005	±·078	66·5	29·7	3·8	·28	·32

It is seen there that the average difference varies from + ·021 with from 1 to 2 per cent. of fat to —·046 with from 4 to 5 per cent. of fat; the total average difference is —·005 per cent.

In Table I. I have rejected 12 analyses, in fact all those milks containing solids-not-fat exceeding 9·5 per cent. as I find that the results calculate too high.

In Table II. I give the whole of the analyses arranged according to percentages of solids-not-fat; those below 8·5 I have grouped together, as these are almost all watered samples; of the others it is seen that the fat calculated exceeds the fat found in proportion as the solids-not-fat rise; the relation between the error and the solids-not-fat is expressed by the formula: Error = ·2 (SNF — 8·87); there is no error when the solids-not-fat are 8·87 per cent., which is almost exactly the mean of Vieth's analyses (The Analyst, xvii., 84).

TABLE II.

Percentage of Solids not Fat.	Number of Samples.	Average error.	Calculated error.
Below 8·5	110	—·032	—
8·5 to 8·75	67	—·053	—.049
8·75 to 9·0	79	+·002	·0
9·0 to 9·25	46	+·044	+·051
9·25 to 9·5	14	+·091	+·101
Above 9·5	12	+·191	+.186

The formula proposed by me (THE ANALYST, xiv., 121), does not give such a good agreement as that of Hehner and myself, on which the milk scale is based, though theoretically more correct; the results by the new formula are ·03 lower, and I can find no other formula which does agree so well as the milk scale.

I do not understand why this is so, as the formula of Hehner and myself assumes that volume-percentages and weight-percentages bear a constant relation, whatever the density may be; of course with the small variations in density found in milk, this error is very small, but it is not entirely negligible, as in extreme cases a difference of ·05 per cent. may be observed.

Table II. to some extent explains the differences of average error with varying percentages of fat; unfortunately the presence of many watered milks renders comparison difficult; two of the columns in Table I. (1 per cent. to 2 per cent. and 4 per cent. to 5 per cent.) each only contain two watered milks and these watered milks differ but very slightly in the fat found and calculated. Neglecting these, the average solids-not-fat are 8·95 per cent. and 8·70 per cent. respectively, giving by the formula above, errors of + ·016 per cent. and — ·034 per cent. respectively; curiously these two columns contain the maximum errors, and these agree very nearly with the errors calculated from the solids-not-fat.

I think then the formula may be corrected to read thus:—

$$T - ·254\,G = 1·164\,F' \text{ and } F = F' - ·2\,(SNF - 8·87);$$
$$\text{or } T - ·254\,G = 1·164\,(F + ·2\,[SNF - 8·87])$$

this correction is of no practical importance, and may be entirely neglected in ordinary work, as it is almost always within the limit of experimental error.

The reason for the variation of the error with the solids-not-fat is not quite clear.

It may be due to three causes:—

(i.) A change in density due to variation in average composition of the solids-not-fat.

(ii.) Incomplete extraction of the fat.

(iii.) An unrecognised phenomenon.

(i.) It is well known that when a cow gives a milk containing a large amount of solids-not-fat, these solids-not-fat do not have an average composition, but include an excess of albuminoids; in consequence of this the density is lowered, but to explain the variation noticed, a much higher density would be required. I have calculated the necessary composition of the solids-not-fat, to give the required density to explain this for 8·5 per cent., 8·87 per cent., and 9·5 per cent., and find them:

	Sugar.	Albuminoids.	Ash.
8·5 p.c.	4·22	4·03	·75
8·87 p.c.	4·80	3·33	·74
9·5 p.c.	6·49	2·34	·67

These figures quite preclude the possibility of adopting explanation (i.), unless we assume that the ash increases in greater ratio than the other constituents. No reliable data are at hand to prove or disprove this.

(ii.) While being without actual proof, I think the fact that methods differing so widely in principle as those of Adams, Storch, and Schmid—which are all theoretically near perfection—give identical results, militates strongly against the idea that the fat is underestimated by at least ·25 per cent.

(iii.) We must then fall back upon explanation (iii.) that there is an unrecognised phenomenon.

I must frankly confess myself baffled in my search for an explanation, and I have brought this paper before the Society for the purpose of drawing the attention of others to this, in the hope that an adequate explanation may be found; it is possible that the finding of this explanation may considerably aid milk analysis.

This revised formula, when applied to Gamoose milks, gives fairly good results; with goat's milk the calculated fat is about 0·2—0·3 too high.

The Reichert Process and its modifications. (*Collected by H. D. Richmond, from the original papers*). Hehner and Angell (*Butter and its Adulterations, London*, 1874) after showing that butter contained more butyric acid than was (then) generally supposed, attempted to estimate this by distillation, but finally relinquished the method on account of discordant results, due largely to the bumping of the liquid and the use of too strong an acid.

Perkins (THE ANALYST, iv., 142) published a method for distilling the volatile acid; he used oxalic acid to decompose the saponified butter, and distilled to dryness. Probably he did not obtain the whole of the acid.

In the same year, Reichert (*Zeits. f. Anal. Chem.*, xviii., 68) proposed to saponify 2·5 grammes of butter with caustic soda and alcohol, evaporate off the alcohol, add 50 c.c. of water and 20 c.c. dilute sulphuric acid, and to distil 50 c.c. in a weak current of air. This method, though Reichert himself calls it Hehner's method, is now known as the Reichert process. He showed that butters took a constant amount of deci-normal alkali for neutralization, while fats and artificial butters took very small quantities—0·3 c.c., and cocoanut oil took about 3·5 c.c.; he proposed 14·0 c.c. as the mean for genuine butters and 13·0 c.c. as a limit; he showed also that mixtures of butter and margarine took quantities of $\frac{1}{10}$ alkali equivalent to the amount of butter they contained.

Moore (*Chem. News., L.* 268) in 1884, and Caldwell (*Chem. News*, Liii., 19) in 1886 both speak favourably of the method, the former drawing especial attention to the fact that cocoanut oil, which is not detected by other methods, is shown by the Reichert method.

Medicus and Sheerer (*Zeits. f. Anal. Chem.*, xix., 159) used this method to show that butter on being melted and allowed to cool, separates into portions containing more or less volatile acids respectively.

Allen (The Analyst, xii., 13) showed that the distilling vessel did not exercise any influence on the results, but that there was a considerable loss on saponification in an open basin, and recommended a closed flask; this loss was due to the formation of butyric ether, as had been already pointed out by Hehner and Angell (*loc. cit.*). Wanklyn and Fox actually estimated the butyric ether formed by saponifying with a barely sufficient quantity of soda (The Analyst, ix., 73), but naturally always fell far below the total quantity.

Munier (*Zeits. f. Anal. Chem.*, xxi., 394) proposed the use of an alcoholic potash solution for saponification and phosphoric acid to liberate the acids.

The results found by various observers are given in the following table:—

Name.	No. of Samples.	Limits.
Reichert (*loc. cit.*)...	13	13·0 — 14·95
Caldwell	?	12·7 — 15·5
Schmitt	?	13·0 — 14·3
Allen (The Analyst, x., 103)	?	12·5 — 15·1
Ambuhl (*Zeits. f. Anal. Chem.*, xix., 159) ...	?	14·05 — 15·55
Munier (*loc. cit.*)	66	9·2 — 14·05
Reichardt (*Zeits. f. Anal. Chem.*, xxiii., 565) ...	35	13·8 — 14·7
Beckhurts (*Jahr. d. Chem. Tech.*, 1883, 978) ...	?	15·6 — 17·5
Merckling (*Pharm. Zeit.*, 1882, 643)	?	13·2 — 13·55
Woll (*Zeits. f. Anal. Chem.*, xxvi., 28)	10	12·0 — 14·9
Cornwall and Wallace (*Ditto* xxvi., 28)... ...	80	11·3 — 15·1
Nilson (*Centralb. f. Agrikulturchemie*, 1887, 171)	?	9·27 — 20·5

Too much importance must not be attached to these figures, as they were obtained by the original form of the method (or very slight modifications); Munier's low results have been criticised by Wollny (*post*), and Nilson's have also been doubted, though on no very strong grounds.

Nilson showed that disease may seriously reduce the volatile acids; one cow whose butter gave 16·85 c.c., after a few day's illness yielded butter taking only 10·1 c.c. of $\frac{N}{10}$ alkali. His lowest result, 9·27 c.c., was obtained from butter prepared from the milk of a cow directly after parturition, and he shows that the quantity of volatile acids rapidly increases, and becomes normal a very short time after calving. Figures as low as 9·27 can then hardly be considered normal for commercial butter.

Meissl (*Dingl. Pol. Journ.*, 233, 229) proposed to saponify 5 grammes of butter-fat in a flask of about 200 c.c. capacity with 2 grammes of caustic potash and 50 c.c. of 70 per cent. alcohol, and to drive off the alcohol on the water bath. The resulting soap

is dissolved in 100 c.c. of water, and 40 c.c. of dilute sulphuric acid (1 to 10) are added and the solution distilled with a few small pieces of pumice; 110 c.c. are collected, filtered, and 100 c.c. titrated with deci-normal alkali. In common with Reichert and the earlier experimenters, he used litmus as an indicator, but the superiority of phenol-phthalein for this purpose soon became apparent to many. To the number of cubic centimetres of $\frac{N}{10}$ alkali one tenth is added; he found thus that butters gave from 26·6 c.c. to 31·8 c.c., and fats and artificial butters about 3·0 c.c.

Sendtner (*Rep. d. Anal. Chem.*, i., 137) as early as 1883 proposed 23 c.c. as the lowest limit.

Hansenn (*Studien u. d. Chem. Nachweis Fremder Fetten. Butter. Erlangen*, 1884, 26), proposed blowing into the flask in order to drive away the last traces of alcohol, and was one of the earliest to use phenol-phthalein as indicator.

This method was adopted by the Congress of Bavarian Analytical Chemists, at Monaco, in 1883; Meissl's limit of 26 c.c. was, however, considered not to be universally applicable, and 23 c.c. was taken. The Paris Municipal Laboratory also adopt it with the modification of saponifying in an open basin, transferring the soap to a flask, and washing the basin with 100 c.c. of hot water; their limits are stringent: 26 c.c. to 33·5 c.c.

The following figures are published:—

Meissl (*loc. cit.*)	52 samples	26·6 — 31·8
Sendtner (*loc. cit.*)	55 „	24·0 — 32·8
Hager (*Chem. Centr.*, 1886, 495) ...	?	26·0 — 31·0

Wollny, in a now classic memoir (*Milch Zeitung*, 1887: 32, 609; 33, 630; 34, 651; and 35, 669; translated in The Analyst, xii., 201, *et seq.*), studied the errors of the Reichert-Meissl process; these are:—

(1). Error due to the absorption of carbonic acid during the saponification (may amount to + 10 per cent.)

(2). Error due to the formation of ethers during saponification (may amount to — 8 per cent.)

(3). Error due to the formation of ethers during the distillation (may amount to — 5 per cent.)

(4). Error due to the cohesion of the fatty acids during distillation (may in extreme cases amount to — 30 per cent.)

(5). Error due to the shape and size of the distilling vessel and to the time of distillation (may vary the results ± 5 per cent.)

To avoid these errors he lays down the following method of working:—

Five grammes of butter-fat are weighed into a round flask of about 300 c.c. capacity, with a neck 2 c.m. wide and 7 to 8 c.m. long; 2 c.c. of a 50 per cent. soda solution and

10 c.c. of 96 per cent. alcohol are added, and the flask heated for half-an-hour on the water bath under a slanting inverted condenser; between the condenser and the flask is a T piece, which is closed, the limb being turned upwards. At the expiration of half-an-hour the limb of the T piece is opened and turned downwards, and the alcohol distilled off during a quarter-of-an-hour; 100 c.c. of boiling water are added by the T piece, and the flask heated on the water bath till the soap is dissolved. The solution is allowed to cool to 50° or 60°, 40 c.c. of dilute sulphuric acid (25 c.c to a litre; 2 c.c. of soda solution should neutralize about 35 c.c. of this) and 2 pieces of pumice the size of peas are added. The flask is at once furnished with a cork carrying a tube 0·7 c.m. in diameter having 2 c.m. above the cork, a bulb 2 to 2·5 c.m. in diameter; above this the tube is bent at an angle of 120° and 5 c.m. further on again at an angle of 120°; this tube is joined to a condenser by an indiarubber tube. The flask is heated by a very small flame till the fatty acids are all melted, and the flame is then turned up and 110 c.c. distilled off in from 28 to 32 minutes. The distillate is well mixed, and 100 c.c. are filtered off through a dry filter, 1 c.c. of a 0·05 per cent. solution of phenol-phthalein solution in 50 per cent. alcohol added, and the solution titrated with $\frac{N}{10}$ baryta solution. To the figure thus obtained one-tenth is added, and the amount found by a blank experiment subtracted; the blank should not exceed 0·33 c.c.

In order to render this method more sensitive, if possible, for the detection of small quantities of butter in margarine, Hehner proposed the use of 5 c.c. only of alcohol, saponifying (almost instantaneously) in a closed flask, warming for five minutes with occasional shaking, and driving off the alcohol through a narrow tube in a cork, reduced pressure being applied towards the end, and the addition of 100 c.c. of water which has boiled at least half an hour. He finds the blank figure thus to be less than 0·1 c.c., and the same as that given by 100 c.c. of boiled water filtered through a dry filter; other fats and oils give less than 0·06 c.c., and no increase is observed in heating them on the water bath with the soda solution for two hours.

In order to facilitate the melting of the fatty acids, Richmond (THE ANALYST, xiv., 112) proposes lengthening the bulb tube, used by Wollny for distillation, above the bulb to 15 c.m. and placing on it a small condenser, through which water is kept running during the melting of the acids, this being removed during distillation; the same results are obtained by the use of this apparatus as by Wollny's.

Mansfeld (*Milch. Zeitung*, 1888, 15, 281) saponifies in a closed flask for two hours on the water bath with a solution of 56 grammes of potash in 100 grammes of water, no alcohol being used; he operates otherwise as Wollny. His method gives the same results as that due to Wollny. His blank is ·4 c.c. and the extremes are 24·42 to 33·15 for butters and 0·59 to 0.96 for margarines.

Goldman (*Chemiker Zeitung*, 1888, 12, 183; 14, 216, and 20, 317) distills the whole of the volatile acids in a current of steam, collects 600 c.c. of distillate, and titrates

with $\frac{N}{10}$ baryta. He finds as limits 36·24 c.c. to 43·20 for butter, and 0·80 to 0.92 for margarine; duplicates do not differ by more than 0·2 c.c. Two samples gave by this method 36·24 and 36·28 c.c., and by the Reichert-Wollny-Mansfeld process 27·00 and 28·04 c.c. respectively.

Leffmann and Beam (The Analyst, xvi., 153) saponify with 2 c.c. of caustic soda solution in 10 c.c. of glycerine, heating over a naked flame with constant shaking. As in the reaction heat is evolved, care must be exercised; they otherwise operate as Wollny. The results are about 0·2 c.c. higher than Wollny's.

The Reichert-Wollny method is largely adopted in every country except France, and may be considered as a standard method.

In England the proportions of the Reichert method with Wollny's precautions are much used; Richmond (*Staz. Sper. Agraria Ital.*,) has determined the ratio between figures obtained thus, and by the Reichert-Wollny method and finds it to be 2·21 to 2·27, mean 2·23. Were the acid all butyric, the ratio would be 2·167. His experiments show that the volatile acids of butter do not distil as if they consisted solely of butyric acid and its homologues, but indicate the presence of another acid: he suggests lactic acid.

The following limits have been found by various observers :—

Name.	No. Samples.	Limits.
Allen (The Analyst, xv. 4)	2	22·5 — 24·55*
Stein (*quoted by* Allen, *loc. cit.*)	?	25·08 — 31·95
Mansfeld (*loc cit.*)	88	24·42 — 33·15
Besana (*Staz. Sper. Ag. Ital.*, xvi.,)	114	21·8 — 30·19
Sartori („ „)	52	23·59 — 30·79
Vigna („ „)	23	20·68 — 31·79
Spallanzani „ „)	70	20·63 — 30·6
Longi („ „)	26	22·55 — 28·4
Maissen and Rossi „)	20	21·56 — 26·40
Schrodt	—	——
Mayer (*Landw. Verss.* xxxv., 261)	20	20·3 — 33·5
Vieth (The Analyst, xiv., 67, 147; xv. 44; xvi., 62, 172; xvii. 62)	236	20·0 — 32·5
F. Jean (*Rev. Int. d. Falsif.*, 1891, 65) ...	1	20·75

Vieth and Spallanzani have also found in samples obtained under exceptional circumstances, which cannot be considered as commercial butter, as low as 14·7 c.c. and 14·3 c.c. respectively.

* These were very exceptional samples, and hence the figures are not representative of the ordinary composition of butter-fat.

The average of the results of different observers (excluding Vieth, who searched for low samples) shows that out of 100 samples—

3 will probably give over 30 c.c.
85 „ „ „ between 30 c.c. and 26 c.c.
8 „ „ „ „ 26 c.c. and 25 c.c.
3 „ „ „ under 25 c.c.

The absolute lower limit must be fixed at 20 c.c. for butters, but all samples giving below 25 c.c. may be looked upon as suspicious, and with a probability of 3 to 100 against such samples being genuine : 25 c.c. may be adopted as a commercial limit. But it must be remembered that the English law gives all probability to the benefit of an accused person.

H. D. R.

[Note by H. D. R.—Leffmann and Beam's modification has the advantages over the Reichert-Wollny method of yielding a clear distillate and giving a sharper end reaction.]

Butter-fat. M. Schrodt and O. Henzold. (*Landw. Versuchs.*, 1892, xl., 229, through *Chem. Zeit.*)—The authors have examined the butter from a herd of 220 to 230 cows weekly for one year. They have arrived at the following conclusions :—

(1). The content of the butter-fat in volatile fatty acids is dependent upon the period of lactation, and is not influenced by the fodder. Diminution of the quantity of volatile fatty acids occurs as lactation advances.

(2). As a rule, a low proportion of volatile fatty acids, while being independent of the fodder, corresponds with a high proportion of insoluble fatty acids, the co-efficient of refraction being thereby raised.

(3). Some samples of butter-fat have a noticeably low content of volatile fatty acids; no satisfactory reason has yet been assigned for this phenomenon.

(4). In consequence of the low limit that can be fixed for the volatile fatty acids, the determination of these constituents for the purpose of checking sophistication, is not completely conclusive. It is, therefore, advisable to estimate also the insoluble fatty acids, and the co-efficient of refraction.

B. B.

Determination of Aluminium in Steel and Alloys. W. Schoeneis. (*Stahl und Eisen*, 1892, xi., through *Chem. Zeit.*)—Five to ten grams of drillings of the metal are dissolved in nitric acid of sp. gr. 1·2, in a platinum dish, evaporated to dryness, and ignited cautiously until all nitrous fumes have ceased. The oxides thus left are ground in an agate mortar, fused with caustic potash free from alumina in a silver dish, then well extracted with water, the filtrate acidulated with hydrochloric acid and precipitated

with ammonia, the alumina being then collected, ignited and weighed. The alumina thus obtained from basic steel is free from silica, but that from Siemens-Martin steel, crucible steel and ferro-aluminium, is contaminated with that substance, and it is, therefore, removed by subsequent treatment with hydrofluoric acid. The beakers used in the analysis must be boiled out with acid. The results bear out the claim of the process to be considered accurate, and a steel containing 0·01 per cent. of Al can be distinguished with certainty from one free from the metal. The method can be used for copper, bronze, and the like.

B. B.

New Method for Estimating Vanadic Acid. A. Rosenheim and C. Friedheim. (*Zeit. für Anorg. Chem.*, I. 313–317.)—In the presence of allied acids, such as phosphoric, tungstic and molybdic acids, it is very difficult to separate vanadic acid in a weighable form. Hitherto reduction with sulphurous acid and subsequent titration with permanganate, or distillation with hydrochloric acid in presence of potassium bromide and absorption of the evolved halogen in potassium iodide, followed by titration of the liberated iodine, have been the methods generally employed for estimating this acid. But of these two methods the former is inapplicable in presence of molybdic and arsenic acids, and the latter is objectionable as introducing potassium, and thus preventing a determination of the alkalies in the same portion.

The author finds that the reaction, first observed by Berzelius, between vanadic anhydride and oxalic acid takes place exactly according to the equation $V_2 O_5 + H_2 C_2 O_4 = V_2 O_4 + H_2 O + 2 C O_2$; and thus serves as a basis for the quantitative determination of the vanadic acid, even in presence of the above mentioned other acids, neither of them being reduced by oxalic acid.

The vanadate, or mineral containing vanadate, is dissolved with the aid of sulphuric acid, the solution mixed with about an equal volume of saturated oxalic acid solution, and heated with more sulphuric acid, if necessary, in a flask connected with an apparatus for absorbing and weighing the evolved carbon dioxide. Every 48·246 parts of carbon dioxide evolved represent 100 parts of vanadic anhydride. A. G. B.

Estimation of Potassium as Perchlorate. W. Wense. (*Zeits. f. Angew. Chem.* 1892, 233-234.)—The author uses the perchlorate method to his entire satisfaction. (THE ANALYST, 1892, 57.) The perchlorate should be obtained in as granular a form as possible ; to this end much free acid is first eliminated by evaporation to dryness, the residue dissolved, the solution warmed on the water bath, and $1\frac{1}{2}$ to $1\frac{3}{4}$ times as much perchloric acid as is equivalent to the amount of potassium supposed to be present dropped in. Ten to twelve properly granular precipitates can be filtered and washed in an hour,

and four hours will suffice for 13 to 14 determinations. To avoid the precipitation of sulphuric acid when present, evaporate with sufficient perchlorate to decompose all chloride, wash with alcohol as usual, dissolve in hot water, evaporate to dryness and ignite strongly enough to convert the potassium perchlorate into potassium chloride, dissolve in water and estimate the chloride by standard silver solution. The method is cheaper than the platinum process. For 5,000 potash determinations some 20 kilos of potassium chlorate and the same quantity of sulphuric acid would be sufficient without recovering the perchloric acid from the precipitates.

A. G. B.

The Estimation of Nicotine in Tobacco-extract. J. Pinette. (*Chem. Zeit.*, xvi., 1072.)—Tobacco-extract is now an article of commerce of considerable importance. It is chiefly used as an insecticide for cattle, and has hitherto been valued by its specific gravity, but a more exact method is now necessary. The determination of the nicotine has been somewhat discredited as a means of valuation, on account of the want of concordance of the results of different analysts. In order to make some advance towards a standard method that may be generally accepted, the author proposes the following process :—

Ten grams of the extract are made up to 50 c.c. and 10 c.c., placed in a graduated separator of 200 c.c. capacity. About 30 c.c. of dilute caustic soda solution are added, and then ether until the total bulk is about 150 c.c. The separator is shaken until the nicotine is all dissolved out by the ether, the volume of the ethereal solution read off, 25 c.c. pipetted into a dish, allowed to evaporate spontaneously, and titrated with decinormal sulphuric acid, using cochineal as an indicator. 1 c.c. of the acid equals 0·0162 grms. of nicotine. The samples examined used 0·2 to 1·8 c.c. of acid, the content of nicotine therefore ranged from 1 to 9 per cent.

The following method, which is, however, considerably more laborious, was used to check the results. 10 grms. of the sample are diluted, made alkaline and distilled in a current of steam, until the distillate measures about 500 c.c. It is then made slightly acid with sulphuric acid, evaporated to about 25 c.c., and titrated with potassium mercuric iodide solution. The latter is prepared according to Kissling's prescription, thus: 87·5 grms. of potassium iodide are dissolved in 250 c.c. of water, and 40 grms. of mercuric chloride in 750 c.c. of (hot) water. The mercuric chloride solution is then poured into the potassium iodide until a permanent precipitate is produced, which is allowed to subside, and removed by filtration through asbestos. The resulting solution measures about 1 litre, and will keep well in the dark. 0·1 gram of nicotine requires 15 to 20 c.c. for precipitation. The exact value is determined by standardizing the solution on pure nicotine under similar conditions. The titration is performed until the addition of the potassium mercuric iodide solution gives no further turbidity. When nearing the end of

the titration, it is best to pour off the clear fluid and add a little more of the reagent, pouring it back again if a precipitate is produced, and shaking it up with the previous precipitate, which induces speedy separation.

B. B.

REVIEW.

Watts' Dictionary of Chemistry:—Revised and entirely re-written by H. Forster Morley, M.A., D.Sc., and M. M. Pattison Muir, M.A. Vol. III. Longmans, Green & Co.

Watts' Dictionary of Chemistry is such a well-known and deservedly appreciated compilation that the appearance of the third volume of the edition now being produced by Professors Morley and Pattison Muir will be welcomed by chemists of every denomination.

The volume under notice contains a number of admirable articles by special contributors, among which that on "Isomerism," by Dr. H. E. Armstrong, and "Metals, Rare," by Mr. William Crookes, deserve honorable mention.

It is to be regretted that all the special articles are not of equal value. Among them stands out prominently, for its imperfections and inaccuracies, that on "Milk," contributed by Dr. W. G. Halliburton, B.Sc., F.R.S. It is unfortunate that an article of such a character should have found a place in the pages of *Watts' Dictionary*.

Referring to the composition of butter, on page 406, Dr. Halliburton states that:—"The fats present are olein, much palmitin, much less stearin; and about 2 per cent. of the total fats consist of the triglycerides of butyric, caproic and caprylic acids, with traces of myristic and arachidic acids. Cow's butter contains about 68 per cent. palmitin and stearin, 30 per cent. olein, and 2 per cent. of the other fats mentioned." Dr. Halliburton is clearly unaware that in the ordinary process of analysis chemists are in the habit of separating over 5 per cent. of volatile acids from butter-fat.

On the succeeding page is a column headed "Analysis of Milk," and in this occur the following methods for determining the solids and butter. "*Solids.*—To 10 grains (*sic*) of dry sand add 5 c.c. of milk, and dry at 100° to constant weight. The increase in weight gives the solids in 5 c.c. of milk. Below 10·5 p.c. of solids in cow's milk indicates dilution. *Butter.*—This may be estimated by weighing the amount of residue from an ethereal extract of milk to which an equal volume of 10 p.c. caustic potash has been added. The normal minimum for fat is about 2·75 p.c. (Cameron)." This is the sum of the information given on the subject of estimation of total solids and fat in milk, and certainly cannot be said to do the subject justice. By public analysts, and other readers of THE ANALYST, such statements would be simply the subject of ridicule, were it not that their occurrence in a standard compilation like *Watts' Dictionary* is likely to be fraught with permanent mischief.

The Editors have, in the present edition, systematically relegated analytical processes to another place, simply recommending the readers to "consult Manuals of Analysis." The wisdom of this policy is fairly open to question, and many besides professional analytical chemists have had cause to lament the absence from the new edition of *Watts' Dictionary* of the full information on analytical matters which was a valuable feature of the first edition. But where analytical processes are described at all, care should be taken that they are described accurately. Possibly editorial revision of Dr. Halliburton's article was considered unnecessary; but in the case of articles contributed by the Editors themselves, the same excuse does not apply. Thus the methods of estimating manganese, as given on page 179, afford a remarkable instance of the slovenly manner in which analytical facts are treated. There the readers are told that "Mn is usually estimated gravimetrically by ppn with NH_3aq, heating the ppt in air and weighing as Mn_3O_4." Even tyros in analysis will open their eyes at being directed to precipitate manganese with ammonia!

On page 124, in reference to the detection of lead, it is stated that "the H_2S test is said to detect 1 pt. of lead in 100,000 pts. of water; the H_2SO_4 test 1 pt. in 20,000; and the K_2CrO_4 test 1 pt. in 70,000."

Surely it should be well known that one-tenth of the quantity of lead said to be recognisable by sulphuretted hydrogen and chromate of potassium can be readily detected by the simple addition of the reagent to the liquid, without using any special device to increase the delicacy of the tests. Again, it should be obvious to the editors of Watts' Dictionary that a test which detected only one grain or two-thirds of a grain of lead per gallon of water would be practically valueless.

Unfortunately the same weakness of description is to be found in other directions besides that of analytical methods. Thus, under the head of phenol, the behaviour of the substance with neutral solvents is limited to statements of its behaviour with water, alcohol and ether; and even then the solubility in water is seriously misstated. But in the last respect the editors only err in company with most other authorities, including Beilstein. The reader is left wholly without information as to the behaviour of phenol with such solvents as chloroform, benzene, petroleum ether, or oils; nor do the editors appear to think the well-known crystalline compound of phenol with water, of the formula $2C_6H_6O+H_2O$, discovered and habitually manufactured by Mr. Charles Lowe, worthy of mention.

Of course *Watts' Dictionary* is indispensable to the advanced student of chemistry; but it is to be regretted that, having gleaned all he can from its pages on a particular subject, he will have to verify and supplement the information by reference to other works of a far less pretentious kind. That such should be the case is to be lamented on every ground, especially since new editions of *Watts' Dictionary* are not produced every day.